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(54) Protected enzyme formulations for use in detergent compositions

(57) A protected enzyme system suitable for storage, prior to use, in a medium such as a liquid detergent which causes degradation of the unprotected enzyme, comprises an enzyme dispersed in a hydrophobic substance which does not dissolve on storage and which is liquid under the conditions of use, or the enzyme may be encapsulated in on or coated with a hydrophobic substance such as petroleum jelly. The enzymes may be those used in detergent compositions.

GB 2 186 884 A

SPECIFICATION

Protected enzyme systems

The present invention relates to protected enzyme systems which are suitable for storage or use in environments which tend to cause degradation of enzymes, such as liquid laundry detergents.

Enzymes are commonly employed as stain removing agents in powder detergents, but their incorporation in liquid cleaning preparations including liquid laundry detergents, such as those described for example in GB 2123846 and GB 2153380 has hitherto presented serious problems. Those liquid formulations which are most effective for soil removal cause rapid degradation of washing enzymes, often resulting in significant loss of stain removing properties after only a few days of storage. The relatively high alkalinity of the more effective soil removing formulations and the chemical action of most of the builder systems and surfactants present therein are particularly antagonistic to detergent enzymes and have largely prevented their use in such detergents, but serious deterioration is observed even in comparatively non-alkaline compositions, which have been specially formulated to permit incorporation of enzymes. Even in powder detergents some degradation of enzymes may be observed, especially if the powder is highly alkaline as in mechanical dishwashing powders, or contains an oxidising bleach such as perborate.

We have now discovered that the deterioration of enzymes in hostile environments such as liquid detergents is substantially reduced when the enzymes are dispersed in a hydrophobic material provided that the latter is insoluble in the particular environment. We have discovered, moreover, that the protected enzyme is available to perform its normal function provided that the hydrophobic material is sufficiently fluid or friable to be disrupted under the conditions of use.

According to one embodiment, therefore, our invention provides a protected enzyme system for storage prior to use, in an environment which causes progressive degradation of unprotected enzymes, said system consisting essentially of a dispersion of at least one enzyme in a hydrophobic substance which is insoluble in the said environment, and which is sufficiently fluid or friable to be disrupted under the normal conditions of use.

According to a preferred aspect our invention provides a protected enzyme system for use in a liquid cleaning composition said system comprising at least one detergent enzyme dispersed in a hydrophobic substance which is insoluble in the liquid detergent but dispersible therein as particles or droplets, and which is sufficiently fluid or friable to be disrupted under cleaning conditions.

According to a second embodiment our invention provides a protected enzyme system for use in a liquid cleaning composition consisting essentially of granules comprising at least one detergent enzyme encapsulated within a hydrophobic substance which is not soluble in the liquid cleaning composition and which is fluid or friable at normal wash temperatures.

According to a third embodiment our invention provides a protected enzyme system for use in liquid detergent compositions consisting essentially of a dispersion of a detergent enzyme in a hydrophobic liquid which is insoluble in liquid detergent.

According to a fourth embodiment our invention provides a method of protecting an enzyme for storage prior to use in an environment which tends to cause progressive degradation of unprotected enzymes, which method comprises dispersing the enzyme in a hydrophobic medium which is insoluble in said environment but dispersible therein as particles or droplets and which is fluid or friable under the normal conditions of use.

According to a fifth embodiment our invention provides a method of protecting enzymes which comprises dispersing a detergent enzyme in a hydrophobic substance which is insoluble in liquid detergent, and fluid at normal wash temperatures.

According to a sixth embodiment our invention provides a liquid cleaning composition having dispersed therein particles or droplets of a protected enzyme system of our invention as hereinbefore described.

References herein to solubility in a medium refer to both dissolution in an aqueous or other continuous solvent phase of the medium and solubilisation in surfactant micelles or any other discontinuous phase dispersed in the medium.

The hydrophobic material may be an organo polysiloxane oil, e.g. a poly di(alkyl)siloxane, wherein the alkyl group has preferably from 1 to 4 carbon atoms, especially a poly di(methyl)siloxane. Especially preferred are hydrophobic liquids which have been stabilised by suspending therein hydrophobic solid particles. Examples include the silicone compositions which have been proposed for use as antifoam in liquid detergents which comprise hydrophobic silicone oil and hydrophobic silica, e.g. a finely divided silica with a silicone at least partly bonded to the surface of the silica particles. For example a hydroxy functional organosiloxane may be condensed with the hydroxy groups of the silica surface. Examples of such compositions include those sold under the Registered Trade Marks "WACKER" Antifoam S132, "BEVALOID" 4237, "UNION

CARBIDE" Y1206, or DIAMOND SHAMROCK'S "NOPCO" 8315. The silicone antifoam may be diluted with an unmodified silicone oil such as a poly dimethyl siloxane. Furthermore the viscosity of the silicone may be increased by addition of finely divided silica eg, fumed silica such as Degussa's "Aerosil" 200 (RTM).

Alternatively the hydrophobic material may be a high molecular weight hydrocarbon, e.g. petroleum bright stock or a so-called petroleum jelly, a high molecular weight alcohol, e.g. more than 28 carbon atoms or a high molecular weight fluocarbon or a hydrophobic phosphate ester such as a mono- and/or di- fatty alkyl phosphate ester or a salt thereof, especially a sodium or calcium salt or a trialkyl or triaryl phosphate. Hydrophobic fluid materials may be further stabilised by inclusion of hydrophobic solid particles, e.g. those formed by condensing silica with silicone as described above or with a fatty alcohol. According to one embodiment the hydrophobic material may be a solid or waxy material at ambient temperature, which has a softening or preferably melting point below normal wash temperature, e.g. below 60°C, preferably below 50°C more usually 40°C, often below 30°C. Such solid materials provide products which are particularly suitable for use in powder as well as liquid detergents. Typically we prefer that our hydrophobic material has a viscosity greater than 0.05 Pascal seconds at normal storage temperature (e.g. room temperature) preferably greater than 0.2, more preferably greater than 0.5 and most preferably greater than 0.8 Pascal seconds. In particular we prefer that the viscosity should be greater than 1 Pascal second e.g. greater than 2 Pascal seconds, especially greater than 10 Pascal seconds. We prefer that the viscosity should be less than 200 Pascal seconds, most preferably less than 100 Pascal seconds, e.g. less than 60 Pascal seconds and especially less than 40 Pascal seconds, at the temperature of use. Fluid materials having a viscosity between 1 and 50 Pascal seconds at ambient temperature are especially suitable.

Unless stated to the contrary, all references herein to viscosities are as measured at 24 sec^{-1} shear and at 25°C.

The enzyme may for example be a detergent enzyme, such as a protease, lipase, amylase, decarboxylase, or cellulase, such as those sold by Novo Industri AS under the Registered Trade Marks "SAVINASE", "TERMAMYL", "ESPERASE" and "ALCALASE", or other enzymes which are active in the removal or amelioration of soil or stains or a mixture of such enzymes.

The enzyme may be present in the hydrophobic material in the form of dispersed droplets of a solution of enzyme, e.g. in water or a lower, preferably water miscible, mono-, di- or polyhydric alcohol such as propylene glycol and optionally containing an enzyme stabiliser such as is known in the art. Enzyme stabilisers which may be present include lower alcohols, e.g. glycerol, lower mono- or di-carboxylic acids and their salts, especially formates and oxalates, borates and calcium salts.

Alternatively the enzyme may be present in the form of suspended particles of an enzyme-containing solid, the solid enzyme being preferably obtained by drying or precipitation from an enzyme solution, optionally containing a stabiliser as aforesaid, e.g. as described in US 3 723 250, particularly at column 12; EP 0 006 638, Example 2a and b GB 1,296,839; U.S. 4,435,307; EP 0 130 064 or Belgian Patent 889336.

The enzyme may also be present in a water soluble granule or marume. Typically this is the form in which enzymes are sold commercially. Thus a soluble crystalline carbohydrate such as sucrose or a salt such as sodium chloride, sodium carbonate or sodium sulphate may be granulated or marumerised with the enzyme, and, optionally, with enzyme stabilisers, e.g. as described in U.S. 4,106,991 or GB 1,362,365, page 9, and the product dispersed in, or coated with, silicone or a hydrocarbon, such as petroleum jelly.

The enzyme may be incorporated in the inert oil by dispersion by simple stirring. Where the hydrophobic material is solid at room temperature it may first be melted before dispersing the enzymes and subsequently cooled to room temperature. Optionally the dispersion may be spray cooled to provide a particulate product.

The proportion of enzyme in the protected enzyme system may be determined by the desired viscosity of the system, where it is desired to handle or store the latter as a liquid. Higher proportions tend to provide higher viscosities, but are less prone to sedimentation of the dispersed enzyme. However, we do not exclude the use of sedimenting systems provided that the enzymes can be easily redispersed by stirring before the system is added to the detergent composition.

Preferably the particle size and proportion of the enzyme are chosen to provide an overall viscosity of the protected system greater than 0.1 Pascal seconds, typically greater than 0.5 Pascal seconds especially greater than 1 Pascal second more preferably greater than 2 Pascal seconds, e.g. greater than 3 Pascal seconds and optionally greater than 10 Pascal seconds, under the conditions of storage and less than 200 Pascal seconds, more preferably less than 100 Pascal seconds, e.g. less than 70 Pascal seconds under the conditions of use. Systems having a viscosity in the range of 2 to 60 Pascal seconds at ambient temperature are generally preferred.

Where enzyme is incorporated in the system as a solution, the solution preferably contains 1

to 90% by weight of enzyme concentrate, e.g. 2 to 80%, typically 5 to 60%, and its dispersion in the oil typically contains 1–80, more usually 5–70, preferably 10–60, more preferably 15–50, e.g. 20–40 or 30–50% by weight of enzyme solution, the percentages being expressed by weight of the total protected enzyme system. The suspension of solid enzyme concentrate in the hydrophobic material typically contains 1 to 90, more usually 5 to 80, preferably 20–60, e.g. 30–50 or 20–30% by weight of solid, based on the total weight of suspension.

The proportion of enzyme in the protected enzyme system may depend on whether the hydrophobic substance is required to perform any useful function in its own right, e.g. as antifoam. Where a low foaming composition is required the enzyme and antifoam may conveniently be in the same relative proportions as those which are required in the final composition. Alternatively a more concentrated suspension of enzyme may be prepared and diluted with more antifoam prior to use, or added to the composition simultaneously with or separately from the additional antifoam.

Where the hydrophobic material is not required to perform a useful function other than protecting enzyme, the enzyme concentration may be the maximum which is consistent with a manageable product.

The particle size of the dispersed enzyme in the protected enzyme system can vary within wide limits. Typically the dispersed enzyme may have a particle size in the range 1μ to 2mm, preferably 5μ to 1mm, e.g. 10μ–700μ. Solid enzyme concentrates tend to be in the lower part of the above range, liquid solutions are normally dispersed with a particle size in the middle of the range, e.g. 100μ–800μ. Granular enzymes usually have a particle size in the upper part of the range, e.g. 300μ–1mm.

The protected enzyme system is generally readily dispersed in the liquid detergent by simple stirring. The system may be dispersed as particles or droplets of from 2μ to 2.5mm diameter, more usually 5μ–500μ, preferably 10μ–100μ, where a dispersed solution or concentrate of enzyme is used as the protected system. Where the enzyme is present as a granulate, the preferred particle size of the system in the liquid detergent is 500μ to 1mm.

Dispersants and emulsifiers may be used as required but are not usually preferred.

Preferably the composition is added to a liquid detergent which comprises an aqueous phase, surfactant, sufficient electrolyte dissolved in the aqueous phase to form with the surfactant, a structure capable of supporting suspended particles, and a protected enzyme system of our invention, suspended in the detergent composition.

Preferably the composition contains an effective amount of a detergent builder. Suitable builders include condensed phosphates, especially sodium tripolyphosphate or, less preferably, potassium pyrophosphate or sodium tetraphosphate, sodium carbonate, sodium silicate, sodium orthophosphate, sodium citrate, sodium nitrilotriacetate, a phosphonate such as sodium ethylenediamine tetramethylene phosphonate, sodium aceto diphosphonate or sodium aminotris (methylene phosphonate), sodium ethylenediamine tetracetate or a zeolite. Other less preferred builders include potassium or lithium analogues of the above sodium salts.

The proportion of builder is typically from about 5% to about 40% by weight of the liquid detergent composition usually 10% to 35%, preferably 15%–30%, more preferably 18% to 28%, most preferably 20 to 27%. Mixtures of two or more builders are often employed, e.g. sodium tripolyphosphate with sodium silicate and/or sodium carbonate, or with zeolite, or sodium nitrilotriacetate with sodium citrate.

Preferably the builder is at least partly present as solid particles suspended in the composition.

Particularly preferred are liquid detergent compositions according to the aforesaid GB 2,123,846 or GB 2,153,380.

The invention is also applicable to the preparation of unbuilt cleaning compositions or compositions in which all the builder is present in solution.

The surfactant may be an anionic, nonionic, cationic, amphoteric, zwitterionic and/or semi polar surfactant which may typically be present in concentrations of from 2 to 35% by weight of the composition, preferably 5 to 30%, more usually 7 to 25%, e.g. 10 to 20%.

Usually the composition contains an alkyl benzene sulphonate together with one or more other surfactants such as an alkyl polyoxyalkylene sulphate and/or a non-ionic surfactant. The latter may typically be an alkanolamide or a polyoxyalkylated alcohol.

Other anionic surfactants include alkyl sulphate, alkane sulphonates, olefin sulphonate, fatty ester, sulphonates, soaps, alkyl sulphosuccinates, alkyl sulphosuccinamates, taurides isethionates and polyoxyalkylene derivates of the aforesaid categories of anionic surfactant. In every case the surfactant for use herein has an alkyl group with an average of from 8 to 22 preferably 10 to 20, e.g. 12 to 18 carbon atoms. Alkyl groups are preferably primary and straight chain, however we do not exclude branched chain or secondary alkyl groups. In the case of alcohol based nonionics the branched chain are sometimes preferred.

The surfactant may be wholly or predominantly non ionic, e.g. a polyoxyalkylated alcohol alone or in admixture with a polyoxyalkylene glycol. Other non-ionic surfactants which may be used include polyoxyalkylated derivatives of carboxylic acids, glycerol, sorbitan, alkylphenols, alkylo-

lamides or amine oxides.

All references herein to polyoxyalkylene groups are preferably to polyoxyethylene groups, or less preferably to polyoxypropylene or mixed oxyethylene oxypropylene copolymeric or block copolymeric groups or to such groups with one or more glyceryl groups. Preferably the polyoxyalkylene groups have from 1 to 30, more usually 2 to 20, e.g. 5 to 15, alkyleneoxy units.

Cationic surfactants for use according to our invention include quaternised alkyl amines, amido amines and imidazolines. Amphoteric surfactants include betaines and sulphobetaines.

In general any surfactant referred to in GB 1,123,846, or in "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, may be used.

Preferably the pH of the liquid detergent composition is alkaline, e.g. about 7.5, especially 7.5 to 12 typically 8 to 11, e.g. 9 to 10.5.

Preferably the liquid detergent composition contains dissolved electrolyte. This may comprise a dissolved portion of the builder and/or any other salt, inorganic or organic, which is not itself a surfactant and which salts out the surfactants present from solution (including micellar solution). Examples include sodium chloride, sodium nitrate, sodium bromide, sodium iodide, sodium borate, sodium formate, or sodium acetate, or corresponding potassium salts. Preferably, however, the electrolyte is a salt which is required to perform a useful function in the wash liquor.

The electrolyte may comprise sodium sulphate in minor concentrations, but electrolyte mixtures containing concentrations of sodium sulphate of about 3% or over based on the total weight of the detergent composition, are preferably not used because they give rise to undesirable crystallisation on standing.

The detergent composition may contain any of the usual minor ingredients such as soil suspending agents (e.g. carboxymethyl cellulose), optical brightening agent, perfume, colouring and, optionally, a bleach.

Particularly preferred liquid detergents are those containing long chain, e.g. C_{10-14} linear alkyl benzene sulphonates in an amount of 5–12%, long chain alkyl ether sulphates, e.g. with 1–5 ethyleneoxy units in amount of 0–3%, fatty acid alkanolamides, e.g. diethanolamides in amount of 1–5%, mixtures of mono and di long chain alkyl phosphates in amount of 0–3%, e.g. 0.1–1%, sodium tripolyphosphate (preferably pre-hydrated with from 0.5 to 5% by weight of water) in an amount of 14–30%, e.g. 14–18% or 20–30% and optionally sodium carbonate in an amount of up to 10%, e.g. 5–10%, with the total of sodium tripolyphosphate and carbonate of 20–30%, antiredeposition agents such as sodium carboxymethyl cellulose in amount of 0.05–0.5%, optical brightening agent in amount of 0.05–0.5%, chelating agents, e.g. amino phosphonates such as methylene phosphonates of di and polyamines especially sodium ethylenediamine tetra[methylene phosphonate] or diethylene triamine hexa[methylene phosphonate] optionally present in amount of 0.1–1%, together with conventional additives such as perfume, the remainder being water, the percentages being by weight of the total liquid detergent. The liquid detergent may have a pH of 6 to 13, preferably 7 to 12, more usually 8 to 11, e.g. 9 to 10.5.

The compositions of the invention may typically contain 0.01 to 10%, e.g. 0.05–0.5% by weight of the protected enzyme system.

Our protected enzyme systems are useful as additives to powder cleaning compositions. For instance enzyme dispersed in silicone antifoam or viscous hydrocarbon may be incorporated into a powder laundry detergent. Conventionally such powders may contain surfactant (usually in total amounts of from 5 to 30% by wt.), builder, a solid filler and optionally a bleach. Usually the surfactant comprises a sodium alkyl (preferably C_{12-14} linear) benzene sulphonate in amounts of from 2 to 20%, preferably 5 to 15%, by weight of the total composition and optionally a sodium alkyl (e.g. C_{12-18}) polyoxyethylene (e.g. 2 to 10% mole) sulphate and/or a non-ionic surfactant such as an alkanolamide, e.g. coconut, mono- or di- ethanolamide and/or a polyethoxylated fatty alcohol.

The builder is typically sodium tripolyphosphate although zeolites, sodium carbonate, sodium silicates, sodium citrate, sodium nitrilotriacetate and mixtures thereof may be present as well as or in place of sodium tripolyphosphate. The total amount of builder is usually between 10 and 40% by weight of the total powder, e.g. 20 to 30%.

The filler is typically sodium sulphate which may typically be present in a proportion of from 0 to 60% usually 20 to 50% of the total composition in order to ensure a free flowing powder.

The bleach is normally a peroxy compound especially a perborate or percarbonate.

The powder also usually contains the usual minor ingredients such as soil suspending agent (typically sodium carboxymethyl cellulose) optical brightening agent and perfume and optionally colouring.

Protected enzyme systems according to our invention may be added to machine dishwashing powders, scouring creams and other hard surface cleaners, carpet shampoos, degreasing compositions, oven cleaners, dishwashing liquids, soap powders, laundry pre soak compositions and other cleaning preparations.

Dishwashing powders according to our invention may typically comprise a substantial proportion, e.g. 20 to 60%, preferably 30 to 50%, of an alkali such as a sodium carbonate and a

minor proportion, e.g. 1 to 5%, of surfactant preferably a non-ionic surfactant such as an alkoxylated alcohol, together, optionally but preferably, with a builder such as sodium tripolyphosphate in proportions of up to about 45% by weight of the composition, e.g. 20 to 35%, an alkaline silicate such as sodium metasilicate and an alkaline buffer such as borax. The composition may optionally contain a bleach such as chlorinated trisodium phosphate and from 0.1 to 2% by weight of the protected enzyme system.

Liquid dishwashing compositions of our invention typically comprise highly soluble builders such as potassium pyrophosphate, and/or potassium silicate in a total concentration of 10 to 30% by weight, surfactants, preferably non-ionic in concentrations of 0.2 to 5% by weight and hydrotropes such as sodium xylene sulphonate, sodium toluene sulphonate or sodium benzene sulphonate in concentrations of 1 to 10% by weight.

Hard surface cleaners of our invention may typically comprise 1 to 10%, surfactant, typically non-ionic or anionic/nonionic mixtures, 1 to 10% hydrotrope and 2 to 10% soluble builder such as potassium pyrophosphate. Hard surface cleaners may also optionally comprise abrasives such as silica, or calcium carbonate as arragonite or calcite suspended in a structural liquid.

Carpet shampoos according to our invention may according to our invention comprise relatively high concentrations, e.g. 5 to 20% by weight, of high foaming surfactants such as mixtures of anionic surfactants (e.g. alkyl sulphates) with foaming agents (e.g. alkanolamides).

Oven cleaners according to our invention may be of the caustic type comprising, e.g. 4 to 12% of alkalis such as sodium hydroxide, and typically a high foaming anionic surfactant such as a sodium alkyl ether sulphate, or else of the solvent based type containing e.g. 10 to 30% of a water miscible organic solvent such as a lower mon- di- or polyhydric alcohol or other alcohol, e.g. propylene glycol, and typically a non ionic surfactant, together preferably with a builder such as sodium tripolyphosphate.

Any difficulties in dispersing the protected enzyme system in any of the foregoing liquid formulations is generally avoided by addition of small amounts of conventional dispersants or suspending agents such as soluble gums or polyelectrolytes.

Normal wash conditions for laundry detergents involve temperatures of from 50°C to 60°C and a wash liquor containing about 2 to 15 gm per litre of detergent composition under vigorous agitation. Some detergents, however, are formulated and recommended for use at cool or intermediate wash temperatures (20 to 30 or 30 to 40°C respectively), either for sensitive fabrics or energy saving.

The invention is illustrated by the following Examples.

Example 1

A protease solution, sold under the Registered Trade Mark "Esperase" 8 OL. was dispersed in a mixture of equal parts by weight of an antifoam silicone oil having a viscosity of 22.57 Pascal seconds at 24 sec ^{1} and 25°C which contains a hydroxyl terminated polysiloxane condensed with solid fumed silica, and is sold under the Registered Trade Mark "Wacker" Antifoam S132, and a neutral polysiloxane oil, sold under the Registered Trade Mark "Wacker" AK50. The silicone mixture had a viscosity of 3.4 Pascal seconds. The dispersion produced contained 38% by weight of the enzyme solution, based on the total weight of dispersion and had a viscosity of 11.9 Pascal seconds at 24 sec ^{1} and 25°C.

The dispersion was incorporated by thorough stirring into a liquid built detergent to give the following formulation:

	wt.%
Sodium linear C_{12} alkyl benzene sulphonate	9.3
Sodium linear C_{12-18} alkyl ether sulphate containing an average of 3 ethyleneoxy units per molecule	1.85
Coconut diethanolamide	1.85
Sodium tripolyphosphate	16.7
Sodium carbonate	6.7
Sodium carboxymethyl cellulose	0.9
Optical brightening agent	0.1
Enzyme dispersion	3
pH	10.5–11.0

This formulation was compared with the same formulation without enzyme as Control for stain removal from a test sample of cotton stained with blood, milk and carbon (EMPA 116) at a concentration of 5gl^{-1} in wash water containing 200ppm calcium carbonate at a wash temperature of 60°C for 30 minutes.

The following percentages stain removal were observed:

Control	36%
Freshly prepared formulation	57%
Formulation after standing 22 days at 30°C	52%

Examples 2 and 3

A 25% by weight suspension was prepared by stirring solid "ESPERASE" protease concentrate (prepared as described in U.S. Patent No. 3,723,250 at col. 12) into a silicone oil with a viscosity of 1.83 Pascal seconds, which was sold by Diamond-Shamrock under the Trade Mark "NOPCO 8315" silicone defoamer.

The suspension had a viscosity of 7.32 Pascal seconds and was incorporated into built liquid detergents to give the following formulations:

	Ex.2	*Ex.3*
Sodium dodecyl benzene sulphonate	6%	7%
Sodium linear C_{12-18} alkyl ether sulphate containing an average of 3 ethyleneoxy units per molecule	2%	—
Coconut diethanolamide	1.5%	3%
Mixture of mono and di C_{16-18} alkyl phosphate ester	0.5%	0.5%
Sodium tripolyphosphate	24%	24%
Sodium carboxymethyl cellulose	0.1%	0.1%
Enzyme suspension in silicone oil	1.25%	1.25%
Optical brightening agent	0.2%	0.2%
Diethylene triamine penta(methylene phosphonate) sodium salt	0.5%	0.5%
Perfume	0.3%	0.3%
Water	to 100%	to 100%
pH	about 9.0	about 9.0

The protease activity of the formulation of Example 2 was 15.4 kilo Novo protease units (KNPU) per g.

Examples 4 and 5

In the same manner as in Examples 2 and 3, a 25% by weight suspension of the "ESPERASE" (Reg. Trade Mark) protease solid concentrate in another silicone antifoam oil having a viscosity of 1.22 Pascal seconds ("BEVALOID" 4237) was prepared and incorporated in the built liquid as in Examples 2 and 3 to give the corresponding formulations Examples 4 and 5 respectively. The suspension had a viscosity of 3.66 Pascal seconds.

The protease activity of the formulation of Example 4 was 14.8 KNPU per g.

Storage Stability Tests

The stability of the formulations of Examples 2 and 4 on keeping at 37°C for 5 weeks were determined and compared to that of a corresponding reference formulation to Example 2 with the same amount of enzyme but no silicone oil.

The residual proteolytic activity of each formulation was determined by the dimethylcasein (DMC) method described in Novo Publication AF 101/4-GB. The results are shown in the following table with activity expressed as a percentage of the initial activity of that formulation:

	Residual Activity after time in weeks		
Formulation	2	4	5
Example 2	80%	70%	70%
Example 4	85%	65%	63%
Reference	33%	9%	n.a.

Examples 6 to 13

A number of alternative protected enzyme systems were each prepared by stirring 25% of solid enzyme concentrate into the hydrophobe and tested as shown in the following Table:

Example No	Enzyme	Trade Name of Hydrophobe	Chemical Type of Hydrophobe	Viscosity P Sec. of Hydrophobe	Viscosity of system in P. Sec.
6	"TERMAMYL"*	"BEVALOID"* 4237	Silicone oil+ hydrophobic silica	1.22	2.44
7	"SAVINASE"*	,,	,,	,,	2.74
8	"ALKALASE"*	,,	,,	,,	2.13
9	,,	"WACKER"* S132+ "WACKER"* AK50	,, diluted with silicone oil		9.76
10	"TERMAMYL"*	,,	,,		10.06
11	"ESPERASE"*	"CATANEX"* 79	Petroluem bright stock	1.62	4.09
12	"ESPERASE"*	"VASELINE"*	Petroleum jelly		
13	"ESPERASE"*	"EMPICOL"* 7062P	mixed mono/di C_{16-18} alkyl acid phosphate		
14	"ESPERASE"	"WACKER"* S132	Silicone oil+ hydrophobic silica	22.7	

*Registered Trade Mark.

Each of Examples 6 to 14 was used as the enzyme system in a sample of liquid detergent according to Example 3. Each was found to exhibit substantially improved retention of enzyme activity and stain removal compared with unprotected enzyme on storage for two weeks at ambient temperature.

Example 15

A dishwashing powder has the following formulation:

Fatty alcohol 12 mole ethoxylate (Registered Trade Mark "EMPILAN" KCMP 0705/F)	2%
Sodium tripolyphosphate	30%
Chlorinated trisodium phosphate	9%
Borax	2%
Sodium metasilicate	8%
Example 10	0.5%
Sodium carbonate	balance

Example 16

A dishwashing liquid has the following formulation:

30% Active aqueous sodium xylene sulphonate (Registered Trade Mark "ELTESOL" SX30)	10%
80% active aqueous synthetic alcohol 8 mole ethoxylate (Registered Trade Mark "EMPILAN" KA880)	0.5%
Potassium hydroxide	1%
Tetra potassium pyrophosphate	15%
Potassium silicate	10%
Example 9	0.5%
Water	balance

Example 17

A hard surface cleaner has the following formulation:

30% sodium xylene sulphonate (Registered Trade Mark "ELTESOL" SX30)	10%
80% synthetic alcohol 8 mole ethoxylate (Registered Trade Mark "EMPILAN" KA880)	2%
30% sodium lauryl sulphate (Registered Trade Mark "EMPILAN" SL30)	5%
Tetra potassium pyrophosphate	5%
Example 12	0.5%
Water	balance

Example 18

A carpet shampoo has the following formulation:

14% sodium lauryl sulphate+ 14% lauric monoethanolamide sulphosuccinate (Registered Trade mark "EMPIMIN" 3119)	25.0%
Example 8	0.5%
Water	balance

Example 19

A carpet shampoo has the following formulation:

28% sodium synthetic lauryl sulphate (Registered Trade Mark "EMPICOL" LX 288/5)	36%
Lauric isopropanolamide	2%
Example 13	0.5%
Water	balance

Example 20

An oven cleaner has the following formulation:

Nonylphenyl 9 mole ethoxylate (Registered Trade Mark "EMPILAN" NP9)	15%
Propylene glycol	20%
Sodium tripolyphosphate	10%
Example 7	0.5%
Water	balance

Example 21

An oven cleaner has the following formulation:

27% lauryl ethersulphate (Registered Trade Mark "EMPIMIN" 27/T)	20%
Sodium hydroxide (as solid)	8%
Example 12	0.5%
Water	balance

CLAIMS

1. A protected enzyme system for storage, prior to use, as a discontinuous phase dispersed in an environment which causes progressive degradation of unprotected enzymes, said system comprising a dispersion of at least one enzyme in a hydrophobic material which is substantially

insoluble in the said environment, and which is sufficiently fluid or friable to be disrupted under the normal conditions of use.

2. A protected enzyme system for use in a liquid cleaning composition, said system comprising at least one detergent enzyme dispersed is a hydrophobic substance, which is substantially insoluble in the liquid cleaning composition but dispersible therein as particles or droplets, and which is sufficiently fluid or friable to be disrupted under cleaning conditions.

3. A system according to claim 2, comprising a hydrophilic solution of at least one detergent enzyme dispersed in a hydrophobic liquid.

4. A system according to claim 2 comprising particles of a solid composition which contain at least one detergent enzyme and which are dispersed in a hydrophobic liquid.

5. A protected enzyme system for use in a liquid cleaning composition consisting essentially of granules comprising at least one detergent enzyme encapsulated within a hydrophobic substance which is not substantially soluble in the liquid cleaning composition and which is fluid or friable at normal wash temperatures.

6. A protected enzyme system comprising at least one detergent enzyme dispersed in a hydrophobic substance which is substantially insoluble as herein defined in aqueous based liquid laundry detergents and which has a softening point below 60°C.

7. A protected enzyme system for use in aqueous based liquid detergents, said system comprising at least one detergent enzyme dispersed in a hydrophobic substance which is substantially insoluble in said liquid detergents and which has a melting point below 60°C.

8. A protected enzyme system according to claim 7 wherein said hydrophobic substance has a melting point below 50°C.

9. A system according to claim 8 wherein said hydrophobic substance has a melting point below 40°C.

10. A protected enzyme system consisting essentially of a detergent enzyme dispersed in a hydrophobic liquid which is substantially insoluble in aqueous based liquid laundry detergents.

11. A system according to any foregoing claim wherein the hydrophobic substance has a viscosity greater than 0.8 Pascal seconds at 24 sec ^{1} shear and 25°C.

12. A system according to claim 11, wherein the hydrophobic substance has a viscosity greater than 10 Pascal seconds at 24 sec ^{1} shear and 25°C.

13. A system according to any foregoing claim wherein the hydrophobic substance has a viscosity less than 200 Pascal seconds at 24 sec ^{1} shear and 60°C.

14. A system according to claim 13, wherein the hydrophobic substance has a viscosity less than 60 Pascal seconds at 24 sec ^{1} shear and 60°C.

15. A system according to claim 14, wherein the hydrophobic substance has a viscosity between 1 and 50 Pascal seconds at ambient temperature.

16. A system according to any foregoing claim having a viscosity greater than 2 Pascal seconds at 24 sec ^{1} shear and 25°C.

17. A system according to claim 16 having a viscosity greater than 10 Pascal seconds at 24 sec ^{1} shear and 25°C.

18. A system according to any foregoing claim having a viscosity less than 200 Pascal seconds at 24 sec ^{1} shear and 60°C.

19. A system according to any of claims 16 to 18 having a viscosity of from 2 to 60 Pascal seconds at 24 sec ^{1} shear and 25°C.

20. A protected enzyme system consisting essentially of a water soluble granule containing a detergent enzyme and coated with petroleum jelly.

21. A system according to any of claims 1 to 19 wherein the hydrophobic substance is a hydrocarbon.

22. A system according to claim 21 wherein the hydrophobic substance is petroleum jelly.

23. A system according to any of claims 1 to 19 wherein the hydrophobic material is an organosiloxane polymer.

24. A system according to claim 23, wherein the hydrophobic material is a silicone antifoam.

25. A system according to either of claims 23 and 24 comprising particles of finely divided hydrophobic silica and a silicone oil.

26. A system according to any of claims 1 to 19 wherein the hydrophobic substance is a hydrophobic phosphate ester.

27. A system according to any foregoing claim, wherein said enzyme comprises one or more of a protease, a lipase an amylase and a cellulase.

28. A method of protecting an enzyme for storage, prior to use, as a discontinuous phase dispersed in an environment which tends to degrade unprotected enzymes, which comprises dispersing the enzyme in a hydrophobic material which is insoluble in the said environment, and which is a liquid under the normal conditions of use and dispersing said hydrophobic material in said environment.

29. A method for protecting at least one detergent enzyme for use in a liquid detergent composition which comprises dispersing said enzyme in a hydrophobic material which is sub-

stantially insoluble in said liquid detergent but which is dispersible therein as particles or droplets, and which is liquid under normal washing conditions.

30. A liquid cleaning composition having dispersed therein particles or droplets of a protected enzyme system according to any of claims 1 to 27.

31. A composition according to claim 30 comprising surfactant and water.

32. A liquid cleaning composition according to claim 31 comprising water, a surfactant, sufficient electrolyte dissolved in the composition to form with the surfactant a structure capable of supporting dispersed solid or liquid particles or droplets, and a protected enzyme system according to any of claims 1 to 27, dispersed in the composition.

33. A composition according to claim 32 which contains a builder.

34. A composition according to claim 33 wherein said builder is at least partially present as suspended solid particles.

35. A composition according to any of claims 30 to 34 having an alkaline pH.

36. A composition according to claim 35 having a pH of from 7.5 to 12.

37. A composition according to claim 36 having a pH of from 8 to 11.

38. A composition according to any of claims 30 to 37 wherein the surfactant comprises an anionic and/or a nonionic surfactant.

39. A composition according to claim 38, comprising (i) an alkyl benzene sulphonate, and (ii) an alkyl ether sulphate and/or a nonionic surfactant.

40. A composition according to any of claims 33 to 39, wherein the builder comprises a condensed phosphate, an orthophosphate, a phosphonate, a zeolite, an alkali metal carbonate, an alkali metal silicate, a nitrilotriacetate, a citrate and/or an ethylenediamine tetracetate.

41. A composition according to claim 40, wherein the builder comprises sodium tripolyphosphate.

42. A composition according to any of claims 31 to 41, wherein the electrolyte comprises a dissolved portion of the builder and/or an added water-soluble non-surface active salt which tends to salt surfactant out of solution.

43. A composition according to any of claims 30 to 42, comprising from 5 to 30% by weight of surfactant and from 0.01 to 10% by weight of the protected enzyme system.

44. A composition according to any of claims 33 to 43, containing from 10 to 40% by weight of builder.

45. A composition according to any of claims 30 to 44 which additionally contains at least one of a soil suspending agent, an optical brightener, perfume, a bleach and a colourant.

46. A composition according to claim 45 containing sodium carboxymethyl cellulose.

47. A powder cleaning composition containing a protected enzyme system according to any of claims 1 to 4 and 6 to 27.

48. A detergent powder according to claim 47 containing at least one surfactant, a builder and a solid filler.

49. A detergent powder according to claim 48 containing a bleach.

50. A detergent powder according to any of claims 47 to 49 wherein the surfactant comprises sodium alkyl benzene sulphonate and at least one of an alkylether sulphate and a nonionic surfactant.

51. A composition according to any of claims 48 to 50 wherein the builder comprises sodium tripolyphosphate.

52. A composition according to any of claims 48 to 51 wherein the filler is sodium sulphate.

53. A composition according to any of claims 49 to 52 wherein the bleach is sodium perborate.

54. A mechanical dishwashing powder containing a protected enzyme system according to any of claims 1 to 27.

55. A dishwashing powder according to claim 54 containing from 30 to 60% of alkali.

56. A dishwashing powder according to claim 55 wherein said alkali comprises sodium carbonate.

57. A dishwashing powder according to any of claims 54 to 56 containing from 10 to 40% by weight of sodium tripolyphosphate.

58. A dishwashing powder according to any of claims 54 to 57 containing from 1 to 5% of non-ionic surfactant.

59. A dishwashing powder according to any of claims 54 to 58 containing a silicate.

60. A hard surface cleaner containing a protected enzyme system according to any of claims 1 to 27.

61. A hard surface cleaner according to claim 60 which comprises from 1 to 10% by weight of anionic and/or non-ionic surfactant, from 2 to 15% by weight of dissolved builder and from 1 to 10% by weight of hydrotrope.

62. A hard surface cleaner according to claim 61 wherein said builder is potassium pyrophosphate.

63. A hard surface cleaner according to either of claims 61 and 62 wherein the hydrotrope is

an alkali metal benzene or alkyl benzene, sulphonate having up to 4 aliphatic carbon atoms.

64. A scouring cream according to any of claims 60 to 63.

65. A scouring cream according to claim 64 containing up to 70% by weight of an abrasive suspended therein.

66. A scouring cream according to claim 65 wherein said abrasive is silica or calcium carbonate.

67. An oven cleaner containing a protected enzyme system according to any of claims 1 to 27.

68. An oven cleaner according to claim 67 containing from 2 to 15% by weight of sodium or potassium hydroxide and from 2 to 15% by weight of anionic and/or non-ionic surfactant.

69. An oven cleaner according to claim 67 containing from 5 to 20% by weight of a non-ionic and/or anionic surfactant, from 5 to 40% by weight of a water-miscible liquid lower mono-, di- or poly-hydric alcohol or ether alcohol, and from 5 to 15% by weight of a builder.

70. A carpet shampoo containing a protected enzyme system according to any of claims 1 to 27.

71. A carpet shampoo according to claim 70 comprising from 2 to 20% by weight of anionic and/or non-ionic surfactants.

72. A carpet shampoo according to claim 71 wherein said surfactant is a mixture of an alkyl sulphate and an alkanolamide.

73. A carpet shampoo according to any of claims 70 to 72 containing up to 10% by weight of a water miscible lower mono-, di- or poly-hydric alcohol, or alcohol ether.

74. A protected enzyme system according to any of claims 1 to 27 substantially as described herein with reference to any of the examples.

75. A composition according to any of claims 30 to 47 substantially as described herein with reference to any of the examples.

76. A composition consisting essentially of a detergent enzyme dispersed in a hydrophobic fluid which has a viscosity of from 0.05 to 200 Pascal seconds.

77. A composition according to any of claims 1 to 27 and 76 wherein said hydrophobic fluid has a viscosity of from 0.8 to 200 Pascal seconds.

78. A composition according to claim 77 wherein said hydrophobic fluid has a viscosity of from 1 to 100 Pascal seconds.

79. A composition according to claim 78 wherein said hydrophobic fluid has a viscosity of from 2 to 50 Pascal seconds.

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